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COMPUTATIONAL EVALUATION OF THE FEASIBILITY OF
NITRATING PRECURSORS TO $C_{12}N_{12}O_{12}$.

by

Peter Politzer and M. Edward Grice

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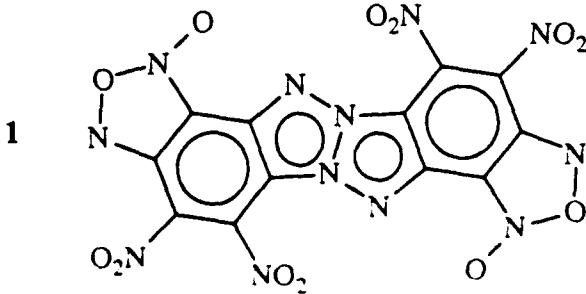
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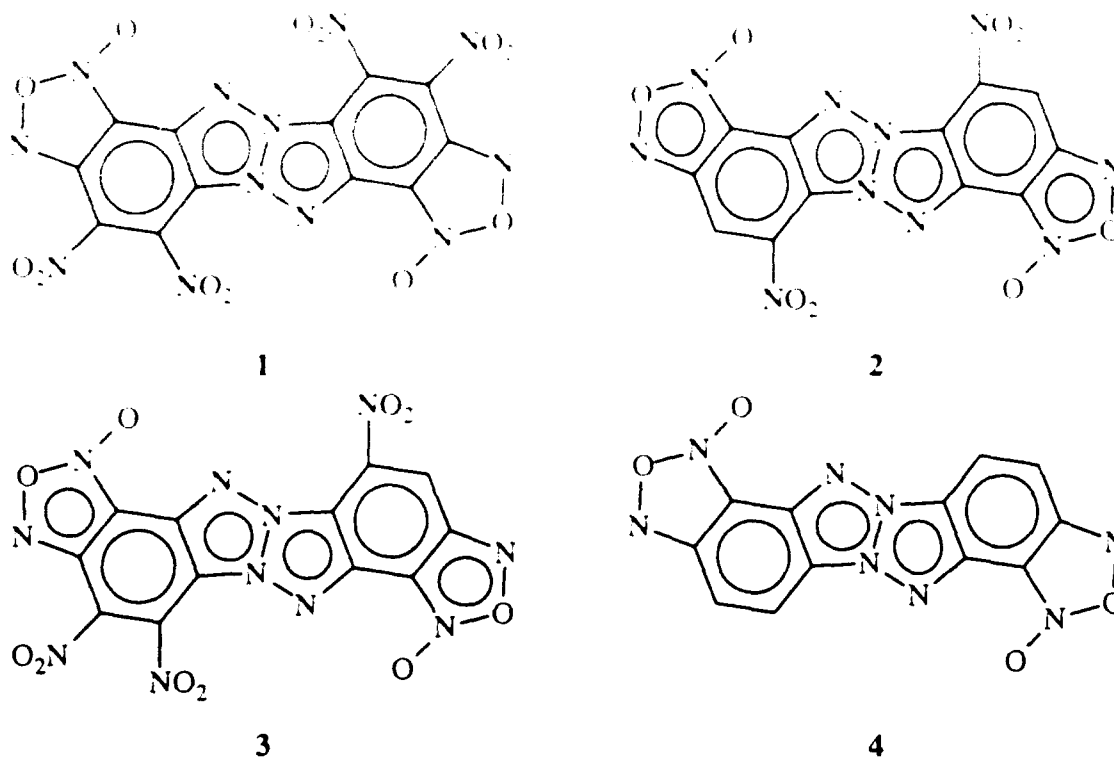
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13. ABSTRACT (Maximum 200 words) In order to determine the feasibility of nitrating the immediate precursors of 1, we have computed the average local ionization energies on their surfaces and compared their minimum values to those of mono-, di- and trinitrobenzene. Our results indicate that there is a reasonable likelihood of being able to nitrate the precursors of 1. <div style="text-align: center; margin: 10px 0;">  <p>1</p> </div>				
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Introduction

In the preparation of **1**, currently underway at the University of New Orleans (J. H. Boyer and M. L. Trudell), possible problems have been encountered in the nitration of the precursor **2**. It is believed that the trinitro derivative **3** is obtained, but there is uncertainty concerning **1**. In response to the suggestion of R. S. Miller, we have investigated the possibility that the electronic properties of **2** and/or **3**, specifically at the unsubstituted carbons, may be unfavorable for the final nitration.



Procedure

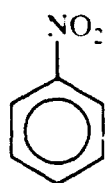
Our approach involved computing the average local ionization energy, $\bar{I}(\mathbf{r})$, on the surfaces of the relevant molecules. $\bar{I}(\mathbf{r})$ is a measure of the average energy required to remove an electron at the point \mathbf{r} . The positions on the molecular surface at which $\bar{I}(\mathbf{r})$ has its lowest values, $\bar{I}_{S,\min}$, are the locations of the most reactive and easily removed electrons, and have been shown to be the sites most susceptible to interactions with electrophiles [1-5], such as NO_2^+ in nitration.

$\bar{I}(\mathbf{r})$ is given by eq. (1) [1],

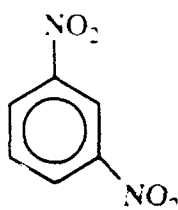
$$I(\mathbf{r}) = \frac{\sum_i \rho_i(\mathbf{r}) |\epsilon_i|}{\rho(\mathbf{r})} \quad (1)$$

in which p_i is the electronic density of the i^{th} molecular orbital, having energy ϵ_i , and $\rho(\mathbf{r})$ is the total electronic density. We define the molecular surface, following Bader *et al* [6], as the 0.001 au contour of $\rho(\mathbf{r})$.

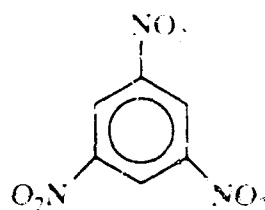
We carried out an *ab initio* HF/6-31G* optimization of the geometry of **1**, using the Gaussian 92 code [7], and then used the same structure for **2**, **3** and **4**, removing the appropriate NO_2 groups. The molecular surface and $\bar{I}_S(\mathbf{r})$ were computed at the HF/STO-5G level, which we have used successfully in the past for these purposes [3,5]. For reference, we also determined the HF/STO-5G $\bar{I}_{S,\text{min}}$ of the nitrobenzenes **5** - **7**, for these calculations we used the experimentally-determined geometry of benzene [8] and added the nitro groups obtained in optimizing **1**. We verified that this does not introduce any inconsistency. Comparing the resulting $\bar{I}_{S,\text{min}}$ for **5** with that obtained earlier for the same molecule using an HF/6-31G* geometry [5], the magnitude was the same, indicating that $\bar{I}_{S,\text{min}}$ is not highly sensitive to the exact geometry used for the calculation.



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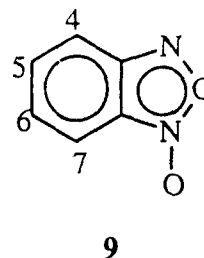
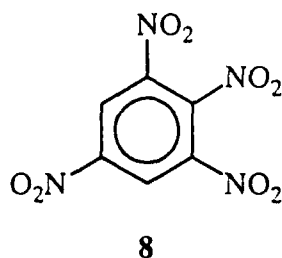
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Results and Discussion

The relevant $\bar{I}_{S,\text{min}}$ are shown in Figure 1. Looking first at the three reference molecules, **5** - **7**, it is seen that in **5** the most reactive position for interaction with an electrophile, as in nitration, is **b** (lowest $\bar{I}_{S,\text{min}}$), while in **6** it is **c**. These conclusions are in accord with the well-established *meta*-directing tendency of the nitro group. As is to be expected, reactivity toward electrophiles decreases in going from **5**, for which the lowest $\bar{I}_{S,\text{min}}$ is 15.1 eV, to **6**, for which it is 15.8 eV. This reflects the strong electron-withdrawing power of the additional NO_2 in **6**. However the direct nitration of **6** to **7** can still be made to occur [9]. There is an even greater increase in $\bar{I}_{S,\text{min}}$ in proceeding to **7**, in which it is 17.2 eV at the ring positions that can be substituted. This is consistent with the known resistance of **7** to further nitration; 1,2,3,5-tetranitrobenzene, **8**, is prepared by indirect means [10].



Molecule 4 is not really relevant to the present discussion because the synthetic pathway introduces the two NO_2 groups of 2 at an early stage in the synthesis, prior to generation of the furoxan rings [11]. It is notable, however, that we find an $\bar{I}_{\text{S,min}}$ at position **b** but not at **a**; this is in agreement with the observation that the preferred site for the nitration of benzofuroxan, 9, is at position 4 (or 7) [12].

In 2, the $\bar{I}_{\text{S,min}}$ at the two unsubstituted carbons (positions **a**) is 16.3 eV; these are accordingly less reactive than the sites in 5 and 6 that are known to undergo direct nitration (positions **b** and **c**, respectively). Nevertheless, nitration at one of the available sites in 2 does occur [11], yielding 3.

It is interesting to note that $\bar{I}_{\text{S,min}}$ at the remaining site in 3, position **a**, is higher in 3 than in 2; evidently the effect of the third NO_2 group is felt despite the four intervening rings! Thus it is more difficult to introduce the fourth NO_2 , and produce 1, than it is to go from 2 to 3. However the difference between the $\bar{I}_{\text{S,min}}$ values in 2 and 3 is small, 0.3 eV (7 kcal/mole), and the $\bar{I}_{\text{S,min}}$ of 3 is still significantly below that of 7, which is known to resist nitration. Accordingly it seems reasonable to continue with efforts to nitrate 3.

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Figure 1. Some Computed (STO-5G) Minima of Average Local Ionization Energies on Molecular Surfaces

